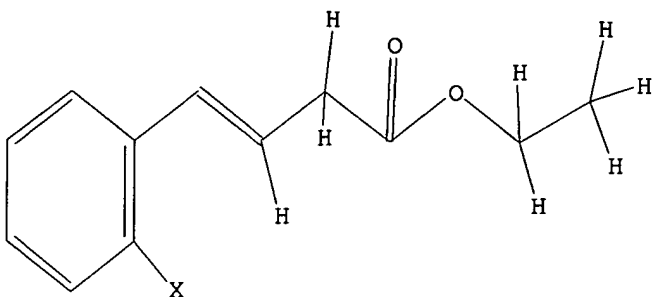


L19, STRUCTURE UPLOADED

=> d

L19 HAS NO ANSWERS

L19 STR



Structure attributes must be viewed using STN Express query preparation.

=> s l19

REGISTRY INITIATED

Substance data SEARCH and crossover from CAS REGISTRY in progress...

Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

SAMPLE SEARCH INITIATED 14:10:34 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 40 TO ITERATE

100.0% PROCESSED 40 ITERATIONS 0 ANSWERS
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED ITERATIONS: 421 TO 1179
PROJECTED ANSWERS: 0 TO 0

L20 0 SEA SSS SAM L19

L21 0 L20

=> s l19 full

REGISTRY INITIATED

Substance data SEARCH and crossover from CAS REGISTRY in progress...

Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

FULL SEARCH INITIATED 14:10:41 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 887 TO ITERATE

100.0% PROCESSED 887 ITERATIONS 4 ANSWERS
SEARCH TIME: 00.00.01

L22 4 SEA SSS FUL L19

=> d 1-4 ibib abs hitstr

L23 ANSWER 1 OF 4 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2005:219834 CAPLUS
 DOCUMENT NUMBER: 142:269572
 TITLE: Cyclopenta[a]naphthalene derivatives for liquid
 crystal display
 INVENTOR(S): Lietzau, Lars; Bremer, Matthias; Klasen-Memmer,
 Melanie
 PATENT ASSIGNEE(S): Merck Patent GmbH, Germany
 SOURCE: PCT Int. Appl., 146 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005021682	A1	20050310	WO 2004-EP8632	20040802
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
DE 102004037387	A1	20050317	DE 2004-102004037387	20040802
PRIORITY APPLN. INFO.:			DE 2003-10338711	A 20030822
OTHER SOURCE(S):	MARPAT	142:269572		

GI

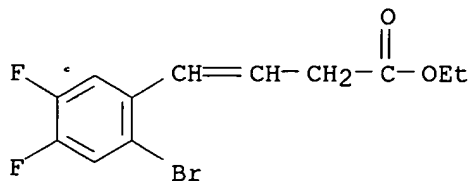
* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB The invention relates to cyclopenta[a]naphthalene derivs. of general
 formulas I, II, III, IV or V (B = (fluoro-substituted) 5-membered ring; A
 = 1,4-phenylene, 1,4-cyclohexylene, etc.; Z = single bond, double bond,
 -CF2O-, -OCF2-, etc.; R = C1-15-alkyl, alkoxy, alkenyl, alkynyl; X1, X1a,
 X1b, X2, X3 = H, C1-15-alkyl, alkoxy, alkenyl, alkynyl; E1, E2 = H,
 C1-15-alkyl, alkoxy, alkenyl, alkynyl; n = 0-3), to the use thereof in
 liquid crystalline media, to liquid crystalline media containing at least one of said
 cyclopenta[a]naphthalene derivs., and to electro-optical display elements
 containing said liquid crystalline media. The synthesis examples are given.

IT **845832-82-8P**
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
 (Reactant or reagent)
 (synthesis of cyclopenta[a]naphthalene derivs. suitable for liquid
 crystal display)

RN 845832-82-8 CAPLUS

CN 3-Butenoic acid, 4-(2-bromo-4,5-difluorophenyl)-, ethyl ester (9CI) (CA
 INDEX NAME)

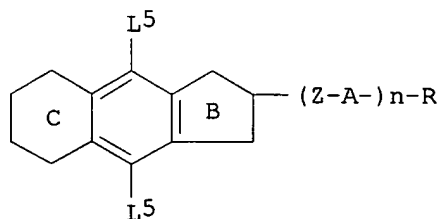


REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L23 ANSWER 2 OF 4 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2004:203786 CAPLUS
 DOCUMENT NUMBER: 140:243724
 TITLE: Cyclopenta[b]naphthalene derivatives
 INVENTOR(S): Lietzau, Lars; Bremer, Matthias; Klasen-Memmer, Melanie; Heckmeier, Michael
 PATENT ASSIGNEE(S): Merck Patent G.m.b.H., Germany
 SOURCE: PCT Int. Appl., 103 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 2
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004020375	A1	20040311	WO 2003-EP8285	20030728
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
DE 10238999	A1	20040304	DE 2002-10238999	20020826
DE 10324843	A1	20041223	DE 2003-10324843	20030602
EP 1532090	A1	20050525	EP 2003-790821	20030728
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK				
JP 2005537334	T2	20051208	JP 2004-569707	20030728
PRIORITY APPLN. INFO.:				
			DE 2002-10238999	A 20020826
			DE 2003-10324843	A 20030602
			WO 2003-EP8285	W 20030728

OTHER SOURCE(S): MARPAT 140:243724
 GI



I

AB The invention relates to cyclopenta[b]naphthalene derivs. of general formula I (C =6-membered ring with substituents selected from H, Cl-15-alkyl, alkoxy, etc.; B = 5-membered ring with substituents selected from H, Cl-15-alkyl, alkoxy, etc.; Z = single bond, double bond, -CF2O-, -OCF2-, etc.; A = 1,4-phenylene, 1,4-cyclohexylene, etc.; R = H,

C1-15-alkyl, alkoxy, etc.; L5, L6 = H, C1-15-alkyl, alkoxy, etc.; n = 0-3), the use thereof in liquid crystal or mesogenous media, liquid crystal or mesogenous media comprising at least one of said cyclopenta[b]naphthalene derivs. and electrooptical display elements comprising said liquid crystal or mesogenous media.

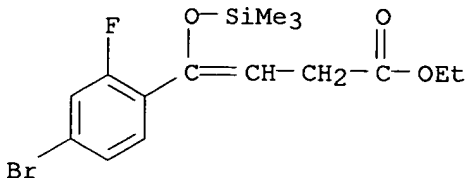
IT **669005-27-0P**

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of cyclopenta[b]naphthalene derivs. suitable for liquid crystal display)

RN 669005-27-0 CAPLUS

CN 3-Butenoic acid, 4-(4-bromo-2-fluorophenyl)-4-[(trimethylsilyl)oxy]-, ethyl ester (9CI) (CA INDEX NAME)



REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L23 ANSWER 3 OF 4 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2003:663938 CAPLUS

DOCUMENT NUMBER: 139:230561

TITLE: Synthesis of Substituted Naphthalenes and Carbazoles by the Palladium-Catalyzed Annulation of Internal Alkynes

AUTHOR(S): Huang, Qinhua; Larock, Richard C.

CORPORATE SOURCE: Department of Chemistry, Iowa State University, Ames, IA, 50011, USA

SOURCE: Journal of Organic Chemistry (2003), 68(19), 7342-7349
CODEN: JOCEAH; ISSN: 0022-3263

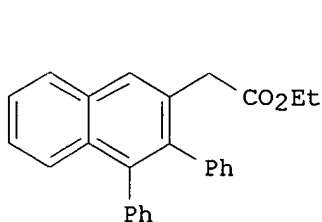
PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

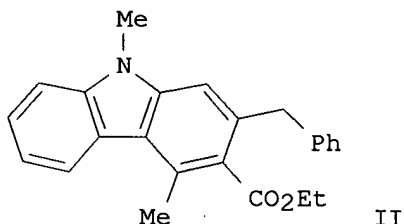
LANGUAGE: English

OTHER SOURCE(S): CASREACT 139:230561

GI



I



II

AB An efficient synthesis of highly substituted naphthalenes has been developed. The palladium-catalyzed annulation of internal alkynes, in which two new carbon-carbon bonds are formed in a single step, under relatively mild reaction conditions, is reported. This method has also been used to synthesize carbazoles, although a higher reaction temperature is required. The process involves arylpalladation of the alkyne, followed by intramol. Heck olefination and double-bond isomerization. This method accommodates a variety of functional groups and affords the anticipated highly substituted naphthalenes, e.g., I, and carbazoles, e.g., II, in good to excellent yields.

IT **593278-17-2P**

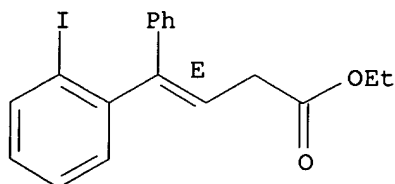
RL: SPN (Synthetic preparation); PREP (Preparation)

(stereoselective preparation of Et (E)-(iodophenyl)butenoates via Wittig reaction of iodobenzophenone followed by hydrolysis, stereoselective Wittig reaction with (carboethoxymethylene)triphenylphosphorane, and double bond isomerization)

RN 593278-17-2 CAPLUS

CN 3-Butenoic acid, 4-(2-iodophenyl)-4-phenyl-, ethyl ester, (3E)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



REFERENCE COUNT: 53 THERE ARE 53 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L23 ANSWER 4 OF 4 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1959:111682 CAPLUS

DOCUMENT NUMBER: 53:111682

ORIGINAL REFERENCE NO.: 53:19988i,19989a-i,19990a-b

TITLE: Experiments on the synthesis of substances related to tetracyclines. IV. Preparation of 4-methyl-8-methoxy-1-naphthol and 1,8-dimethoxy-4-methyl-2-naphthoic acid, two useful intermediates for dedimethylaminotetrarubein synthesis

AUTHOR(S): Huang, Yao-Tseng; Tsung, Hui-Chuan; Tai, Li-Hsin; Sheng, Huai-Yu; Tu, Tung-Yuan

SOURCE: Huaxue Xuebao (1958), 24, 311-22

CODEN: HHHPPA4; ISSN: 0567-7351

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 53, 3171e. 1,8-(HO)2C10H6 (I) (2 g.) was methylated either by Staudinger's method (cf. S., et al., C.A. 15, 3445) to give 1.1 g. 8,1-MeOC10H6OH (II), m. 55°, soluble in hot dilute NaOH, and 0.2 g. 1,8-(MeO)2 C10H6, m. 157-9°, or by refluxing 5 hrs. I (40 g.), 33 g. MeI, and 40 g. anhydrous K2CO3 in 160 ml. Me2CO to give 25.8 g. II. Dry HCl was passed to a mixture of 8.5 g. II, 9 g. freshly prepared Zn(CN)2, and 1.3 g. KCl in 150 ml. Et2O with constant agitation at room temperature for 3 more hrs. beyond saturation and 150 ml. 50% EtOH was added to dissolve the separated solid and to yield on cooling 4.9 g. 4,5,1-HO(MeO)C10H5CHO (III), m. 112.5-13°; semicarbazone m. 244°. By refluxing 2 g. III and 6 g. Zn-Hg 4 hrs. in 15 ml. EtOH and 70 ml. MePh with 14 ml. concentrated HCl dropped in continuously 0.28 g. 4,8,1-Me(MeO)C10H5OH (IV) was obtained, m. 75-6° (MeOH). IV could also be prepared from III by Kishner-Wolff method modified by Huang-Minlon. Bromination of 7 g. IV with 5.94 g. Br in CCl4 at 70° 2.5 hrs. gave 9.28 g. 2,4,8,1-BrMe(MeO)C10H4OH (V), m. 104-5.5° (90% MeOH), which (2.73 g.) was methylated with Me2SO4 in 5% KOH-EtOH solution to yield 1.84 g. 2,4,1,8-BrMeC10H4(OMe)2 (VI), b3 168-78°, m. 44-6° (petr. ether). VI (750 mg.) in 5 ml. absolute Et2O was stirred with freshly prepared BuLi at -20° 10 min., CO2 was passed in, and the mixture was finally acidified with 6N HCl to give 0.37 g. 4,1,8,2-Me(MeO)2C10H4CO2H (VII), m. 121-2.5° (CCl4); the acid chloride m. 167.5-8.5°. In order to ascertain the structures of IV and VII another route to synthesize these compds. was proposed. 2,5-Cl(H2N)C6H3CO2H.HCl (50 g.) in 250 ml. 10% AcOH was diazotized with 15 g. NaNO2 in 125 ml. H2O at 0-5°, kept 1 hr., and boiled with 1.5 l. water to give 20.5 g. 2,5-Cl(HO)C6H3CO2H (VIII), m. 173-6° (3:10 Et2O-petr. ether). Methylation of 34.5 g. VIII in 100 ml. MeOH and 20 g. NaOH with 47 ml. Me2SO4 added dropwise and 28 ml. 50% KOH added at intervals to keep, the solution finally alkaline yielded 76.5%

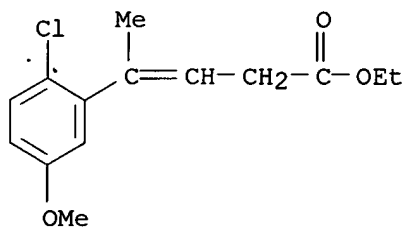
2,5-Cl(MeO)C₆H₃CO₂H, m. 172-3°, which (60 g.) was converted to 94% 2,5-Cl(MeO)C₆H₃COCl (IX), b₅ 126-8°, m. 24-5°, by heating to 70° with 67 g. PCl₅. Addition of 18.3 g. IX in 10 ml. Et₂O to an ether solution of 0.69 g. CH₂N₂ at 0° and keeping at room temperature 2 hrs. gave 2,5-Cl(MeO)C₆H₃COCHN₂, m. 46-7° (ether-petr. ether), from which 2,5-Cl(MeO)C₆H₃COCH₂Cl (X) (95% yield), m. 40°, or 2,5-Cl(MeO)C₆H₃COCH₂Br (Xa) (95% yield), m., 14° was obtained by reaction with HCl or HBr, resp., in ether solution at 0° and room temperature 1 hr. Refluxing 2 g. X in 8 ml. C₆H₆ with CHNa(CO₂Et)₂ [solution of 0.21 g. Na, 20 ml. C₆H₆ and 5 ml. CH₂(CO₂Et)₂] 24 hrs. and hydrolyzing the residue with KOH-MeOH (3.2 g. in 32 ml.) at refluxing temperature 3 hrs. gave 57% 2,5-Cl(MeO)C₆H₃COCH₂CH(CO₂H)₂, m. 170° (Me₂CO-C₆H₆) (decomposition), which decomposed at 180° to 82% 2,5-Cl(MeO)C₆H₃COCH₂CH₂CO₂H (XI), m. 92-3° (C₆H₆). Grignard reaction of 8 g. XI in 150 ml. dry Et₂O and 50 ml. C₆H₆ with MeMgCl (from 2 g. Mg) at room temperature 1 hr., at refluxing temperature 12 hrs. followed by decomposition with 60 ml. 2N HCl gave 86% 2,5-Cl(MeO)C₆H₃CM_e.CH₂.CH₂.CO.O (XII), b_{0.03} 133-4°. By refluxing 14.5 g. XII in 38 ml. dry C₆H₆ with 12.5 ml. SOCl₂ 90 min., keeping overnight with 102 ml. absolute EtOH, and heating at 180° 1 hr., 2,5-Cl(MeO)C₆H₃CM_e:CHCH₂CO₂Et (XIII) was obtained in 86% yield, b_{0.02} 120°. Hydrogenation of 14.5 g. XIII in 100 ml. AcOH with 450 mg. PtO₂ at 30° until 1.46 l. H was absorbed, and hydrolysis of the product with 10 g. KOH in 12 ml. H₂O and 70 ml. MeOH at boiling temperature 2 hrs. gave 77% 2,5-Cl(MeO)-C₆H₃CHMeCH₂CH₂CO₂H, m. 82-3° (petr. ether), which (8.98 g.) cyclized to 91% 4-methyl-5-chloro-8-methoxy derivative of 1-tetralone (XIV), m. 76-7°, when 8.4 g. PCl₅, 9 ml. SnCl₄ (in 9 ml. C₆H₆), and 32 ml. ice-HCl were added in order to the C₆H₆ solution with agitation. Bromination of 200 mg. XIV in CHCl₃ gave the 2-bromo derivative, m. 85-6° (MeOH-H₂O), which (0.2 g.) lost HBr very readily by heating 3 min. with 0.42 g. morpholine to form 69% 4,5,8,1-MeCl(MeO)C₁₀H₄OH, m. 122-3°. This (222 mg.) was finally hydrogenated in 30 ml. EtOH in the presence of 1.5 g. Pd-SrCO₃(2%) in 5 ml. 10% KOH to yield 70% IV. Bromination of 2.4 g. XIV with 2 moles Br (3.36 g.) in CHCl₃ (105 ml.) and keeping overnight gave 80% 2,2-dibromo-4-methyl-5-chloro-8-methoxy derivative of 1-tetralone, m. 129-30° (MeOH-CHCl₃), which was converted into 73% 1,8-dimethoxy-2-bromo-4-methyl-5-chloronaphthalene (XV), m. 87-8°, by refluxing with MeONa-MeOH and Me₂SO₄ added in portions alternately 6-7 times. Chlorination of 0.5 g. VI with 0.126 g. Cl in 8 ml. AcOH or of 100 mg. XV with 25 mg. Cl in 4.5 ml. AcOH at room temperature gave 2,4-dichloro-5-methyl-7-bromo-8-methoxy-1-naphthol, m. 155-7° (AcOH), λ 250, 322, 340, 355 mμ. Refluxing 560 mg. V with EtOK and Et₂SO₄ added in portions alternately yielded 2,4,8,1-BrMe(MeO)C₁₀H₄OEt, b_{0.07} 133.5-8.0°, m. 56-7° (petr. ether), which was chlorinated in AcOH to 2,4-dichloro-5-methyl-7-bromo-8-ethoxy-1-naphthol, m. 117.5-18.5° (AcOH). Attempt to synthesize XI by the condensation of IX and EtO₂CCNaAcCH₂CO₂Et (XVI) followed by hydrolysis was unsuccessful although 5 g. 3-MeOC₆H₄COCl and XVI (0.7 g. Na and 7 g. EtO₂CCHAcCH₂CO₂Et) refluxed 2 hrs., shaken 20 hrs. with 0.6 l. 1.5% KOH, purified by isolation of the product as semicarbazone, m. 179- 80°, and hydrolyzed with 2N HCl 130° gave 3-MeOC₆H₄- COCH₂CH₂CO₂H, m. 107-8.5°.

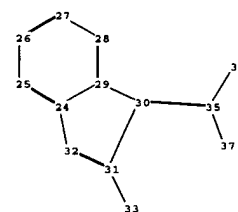
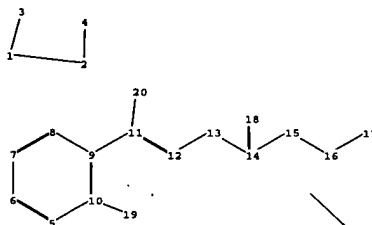
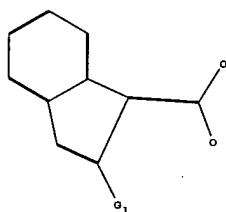
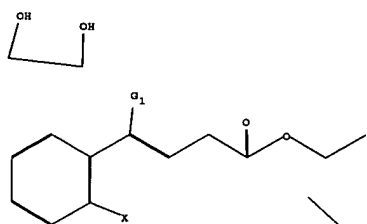
IT 107625-25-2, 3-Pentenoic acid, 4-(2-chloro-5-methoxyphenyl)-, ethyl ester

(preparation of)

RN 107625-25-2 CAPLUS

CN 3-Pentenoic acid, 4-(2-chloro-5-methoxyphenyl)-, ethyl ester (6CI) (CA INDEX NAME)





chain nodes :

1 2 3 4 11 12 13 14 15 16 17 18 19 20 33 35 36 37

ring nodes :

5 6 7 8 9 10 24 25 26 27 28 29 30 31 32

chain bonds :

1-2 1-3 2-4 9-11 10-19 11-12 11-20 12-13 13-14 14-15 14-18 15-16 16-17 30-35
31-33 35-36 35-37

ring bonds :

5-6 5-10 6-7 7-8 8-9 9-10 24-25 24-29 24-32 25-26 26-27 27-28 28-29 29-30
30-31 31-32

exact/norm bonds :

1-3 2-4 11-20 14-15 14-18 15-16 24-32 29-30 30-31 31-32 31-33 35-36 35-37

exact bonds :

1-2 9-11 10-19 11-12 12-13 13-14 16-17 30-35

normalized bonds :

5-6 5-10 6-7 7-8 8-9 9-10 24-25 24-29 25-26 26-27 27-28 28-29

G1: Ph, COOH, CN, OSO₃H, C(O)CH₃, NO₂

Match level :

1:CLASS 2:CLASS 3:CLASS 4:CLASS 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom
11:CLASS 12:CLASS 13:CLASS 14:CLASS 15:CLASS 16:CLASS 17:CLASS 18:CLASS 19:CLASS
20:CLASS 24:Atom 25:Atom 26:Atom 27:Atom 28:Atom 29:Atom 30:Atom 31:Atom 32:Atom
33:CLASS 35:CLASS 36:CLASS 37:CLASS

fragments assigned reactant/reagent role:
containing 5

=>
Uploading C:\Program Files\Stnexp\Queries\4735.str

L1 STRUCTURE UPLOADED

=> d
L1 HAS NO ANSWERS
L1 STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

Structure attributes must be viewed using STN Express query preparation.

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FULL SEARCH INITIATED 13:00:31 FILE 'CASREACT'
SCREENING COMPLETE - 4 REACTIONS TO VERIFY FROM 2 DOCUMENTS

100.0% DONE 4 VERIFIED 0 HIT RXNS 0 DOCS
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SCREENING COMPLETE - 4 REACTIONS TO VERIFY FROM 2 DOCUMENTS

100.0% DONE 4 VERIFIED 0 HIT RXNS 0 DOCS
SEARCH TIME: 00.00.01

L3 0 SEA SSS FUL L1 (0 REACTIONS)

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COST IN U.S. DOLLARS SINCE FILE TOTAL
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FULL ESTIMATED COST 222.48 222.69

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DICTIONARY FILE UPDATES: 7 FEB 2006 HIGHEST RN 873775-18-9

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TSCA INFORMATION NOW CURRENT THROUGH JULY 14, 2005

Please note that search-term pricing does apply when
conducting SmartSELECT searches.

*
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added, *
* effective March 20, 2005. A new display format, IDERL, is now *
* available and contains the CA role and document type information. *
*

Structure search iteration limits have been increased. See HELP SLIMITS
for details.

REGISTRY includes numerically searchable data for experimental and
predicted properties as well as tags indicating availability of
experimental property data in the original document. For information
on property searching in REGISTRY, refer to:

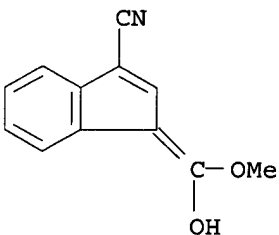
<http://www.cas.org/ONLINE/UG/regprops.html>

=> s 474024-30-1/rn
L4 1 474024-30-1/RN

=> s
ENTER LOGIC EXPRESSION, QUERY NAME, OR (END):end
SEARCH ENDED BY USER

=> d 14

L4 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2006 ACS on STN
RN 474024-30-1 REGISTRY
ED Entered STN: 20 Nov 2002
CN 1H-Indene-3-carbonitrile, 1-(hydroxymethoxymethylene)-, sodium salt (9CI)
(CA INDEX NAME)
MF C12 H9 N O2 . Na
SR CA
LC STN Files: CA, CAPLUS, USPATFULL
CRN (474024-40-3)

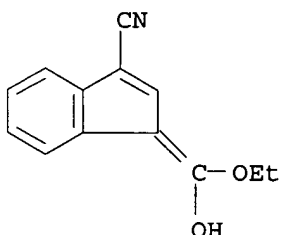


1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 474024-31-2/rn
L5 1 474024-31-2/RN

=> d

L5 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2006 ACS on STN
RN 474024-31-2 REGISTRY
ED Entered STN: 20 Nov 2002
CN 1H-Indene-3-carbonitrile, 1-(ethoxyhydroxymethylene)-, sodium salt (9CI)
(CA INDEX NAME)
MF C13 H11 N O2 . Na
SR CA
LC STN Files: CA, CAPLUS, CASREACT, USPATFULL
CRN (749843-51-4)



● Na

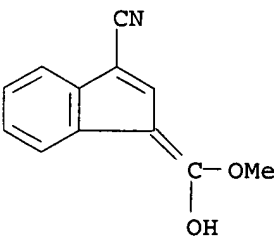
PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

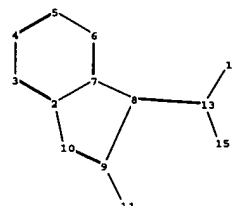
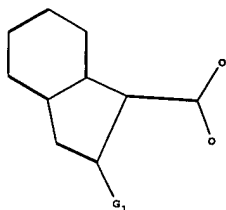
2 REFERENCES IN FILE CA (1907 TO DATE)
2 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 474024-40-3/rn
L6 1 474024-40-3/RN

=> d

L6 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2006 ACS on STN
RN 474024-40-3 REGISTRY
ED Entered STN: 20 Nov 2002
CN 1H-Indene-3-carbonitrile, 1-(hydroxymethoxymethylene)- (9CI) (CA INDEX
NAME)
FS 3D CONCORD
MF C12 H9 N O2
CI COM
SR CA
LC STN Files: CA, CAPLUS, USPATFULL





chain nodes :
 11 13 14 15
 ring nodes :
 2 3 4 5 6 7 8 9 10
 chain bonds :
 8-13 9-11 13-14 13-15
 ring bonds :
 2-3 2-7 2-10 3-4 4-5 5-6 6-7 7-8 8-9 9-10
 exact/norm bonds :
 2-10 7-8 8-9 9-10 9-11 13-14 13-15
 exact bonds :
 8-13
 normalized bonds :
 2-3 2-7 3-4 4-5 5-6 6-7

G1:Ph,COOH,CN,OSO₃H,C(O)CH₃,NO₂

Match level :
 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom 11:CLASS 13:CLASS
 14:CLASS 15:CLASS

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> file caplus

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

9.66

232.81

FILE 'CAPLUS' ENTERED AT 13:09:57 ON 09 FEB 2006

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FILE COVERS 1907 - 9 Feb 2006 VOL 144 ISS 7

FILE LAST UPDATED: 8 Feb 2006 (20060208/ED)

Effective October 17, 2005, revised CAS Information Use Policies apply. They are available for your review at:

<http://www.cas.org/infopolicy.html>

=>

Uploading C:\Program Files\Stnexp\Queries\4735a.str

L7 STRUCTURE UPLOADED

=> d

L7 HAS NO ANSWERS

L7 STR

*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

Structure attributes must be viewed using STN Express query preparation.

=> s 17

REGISTRY INITIATED

Substance data SEARCH and crossover from CAS REGISTRY in progress...

Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

SAMPLE SEARCH INITIATED 13:10:44 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 312 TO ITERATE

100.0% PROCESSED 312 ITERATIONS

0 ANSWERS

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**

BATCH **COMPLETE**

PROJECTED ITERATIONS: 5181 TO 7299

PROJECTED ANSWERS: 0 TO 0

L8 0 SEA SSS SAM L7

L9 0 L8

=> s l7 full

REGISTRY INITIATED

Substance data SEARCH and crossover from CAS REGISTRY in progress...

Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

FULL SEARCH INITIATED 13:11:08 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 6227 TO ITERATE

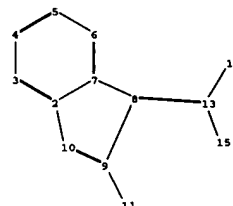
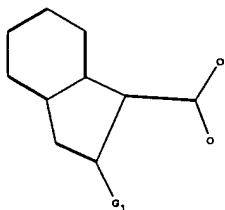
100.0% PROCESSED 6227 ITERATIONS

0 ANSWERS

SEARCH TIME: 00.00.01

L10 0 SEA SSS FUL L7

L11 0 L10



```

chain nodes :
  11 13 14 15
ring nodes :
  2 3 4 5 6 7 8 9 10
chain bonds :
  8-13 9-11 13-14 13-15
ring bonds :
  2-3 2-7 2-10 3-4 4-5 5-6 6-7 7-8 8-9 9-10
exact/norm bonds :
  2-10 7-8 8-9 9-10 9-11 13-14 13-15
exact bonds :
  8-13
normalized bonds :
  2-3 2-7 3-4 4-5 5-6 6-7
  
```

G1:Ph,COOH,CN,OSO3H,C(O)CH3,NO2

```

Match level :
  2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom 11:CLASS 13:CLASS
  14:CLASS 15:CLASS
  
```

=> s 112

REGISTRY INITIATED

Substance data SEARCH and crossover from CAS REGISTRY in progress...

• Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

SAMPLE SEARCH INITIATED 14:06:42 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 3920 TO ITERATE

51.0% PROCESSED 2000 ITERATIONS 2 ANSWERS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.01

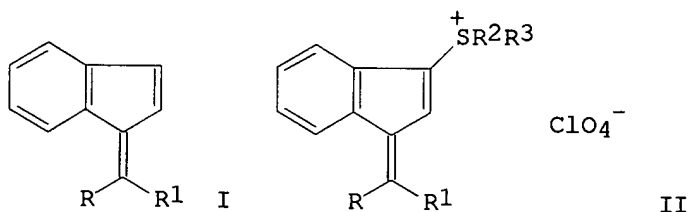
FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED ITERATIONS: 74646 TO 82154
PROJECTED ANSWERS: 2 TO 196

L13 2 SEA SSS SAM L12

L14 1 L13

=> d ibib abs hitstr

L14 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1988:437562 CAPLUS
DOCUMENT NUMBER: 109:37562
TITLE: Electrophilic substitution of benzofulvenes with
activated sulfoxides
AUTHOR(S): Teuber, Dorothee; Hartke, Klaus
CORPORATE SOURCE: Inst. Pharm. Chem., Univ. Marburg, Marburg, D-3550,
Fed. Rep. Ger.
SOURCE: Liebigs Annalen der Chemie (1988), (1), 39-42
CODEN: LACHDL; ISSN: 0170-2041
DOCUMENT TYPE: Journal
LANGUAGE: German
OTHER SOURCE(S): CASREACT 109:37562
GI



AB The benzofulvenes I (R = R1 = Ph, Me, EtO, MeS; R = Me, R1 = Ph) were treated with R2R3SO [R2 = R3 = Me, PhCH2, Ph, p-MeC6H4; R2 = R3 = (CH2)4, CH2CH2OCH2CH2] in presence of (F3CCO)2O followed by aqueous LiClO4 to give the sulfoniobenzofulvene perchlorates II.

IT **115176-52-8P**

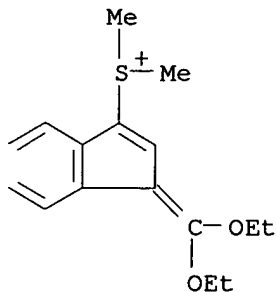
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 115176-52-8 CAPLUS

CN Sulfonium, [1-(diethoxymethylene)-1H-inden-3-yl]dimethyl-, perchlorate
(9CI) (CA INDEX NAME)

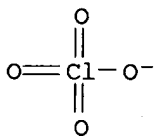
CM 1

CRN 115176-51-7
CMF C16 H21 O2 S



CM 2

CRN 14797-73-0
CMF C1 O4



=> s l12 full

REGISTRY INITIATED

Substance data SEARCH and crossover from CAS REGISTRY in progress...
Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

FULL SEARCH INITIATED 14:07:13 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 78051 TO ITERATE

100.0% PROCESSED 78051 ITERATIONS 39 ANSWERS
SEARCH TIME: 00.00.01

L15 39 SEA SSS FUL L12

L16 23 L15

=> s l14 and py<2002

21804522 PY<2002

L17 1 L14 AND PY<2002

=> s l16 and py<2002

21804522 PY<2002

L18 21 L16 AND PY<2002

=> d 1-21 ibib abs hitstr

L18 ANSWER 1 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2000:667072 CAPLUS

DOCUMENT NUMBER: 133:334870
TITLE: Calculated pKENol Values for β,β -Diarylacetic Acids and β,β -Diarylacetaldehydes. Effect of Steric Bulk of Substituents on the Relative Stability of Enols of Carboxylic Acids and Aldehydes
AUTHOR(S): Yamataka, Hiroshi; Rappoport, Zvi
CORPORATE SOURCE: Institute of Scientific and Industrial Research, Osaka University, Ibaraki Osaka, 567-0047, Japan
SOURCE: Journal of the American Chemical Society (2000), 122(40), 9818-9828
CODEN: JACSAT; ISSN: 0002-7863
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English

AB The energies, pKENol values, structures, and conformations of vinyl alc. (3a), acetaldehyde (4a), 1,1-ethenediol (5a), acetic acid (6a), and six derivs. of each substituted by two β -aryl groups of increasing bulk from Ph to Tip (2,4,6-tri-*i*-PrC₆H₂) were calculated by the B3LYP method in order to evaluate quant. the pKENol reducing effect of bulky aryl groups. Also calculated were the same parameters for the ArCHXCO₂H/ArC(X):C(OH)₂ pairs for Ar = Ph, X = CN (9a/9b), OH (10a/10b), for which pKENol is known, and for Ar = Mes (mesityl), X = CN. All the substituents significantly decrease the pKENol values from 22.4 (6a/5a) and 9.1 (4a/3a). For example, pKENol = 0.2, -2.7, -2.0, and -2.7 for ArAr'CHCHO/ArAr'C:CHOH and 13.3, 11.5, 9.2, and 9.3 for ArAr'CHCO₂H/ArAr'C:C(OH)₂ when Ar, Ar' = Ph, Ph, Ph, Mes, Mes, Mes, and Tip, Tip, resp. For 9a/9b and 10a/10b, the calculated pKENol values resemble the observed ones. The enols and enediols (except 3b and 5b, when Ar₂C: = fluorenylidene) have a propeller conformation. The Ar-C:C torsional angles increase with increasing bulk of the aryl group, but for Ph, bulkier Ar the Ar-C:C torsional angle strongly exceeds the Ph-C:C angle. The syn-C:C-O-H conformer is preferred over the anti conformer for all the enols 3. For the 1,1-enediols, the syn,syn conformer is preferred for most Ar, Ar' combinations, but the syn,anti conformer is preferred for 5a and 5b [ArAr'C=C(OH)₂; Ar = Ph, Ar' = 2,4,6-(*t*-Bu)₃C₆H₂], and 10a, and the anti,anti conformation is the least stable. The stabilization and conformational preferences were analyzed both qual. and with the aid of appropriate isodesmic reactions. Superposition of stabilizing Ar-C:C conjugation effects, stabilization of the carbonyl forms, and π (Ar)···O hydrogen bonding and destabilizing geminal Ar/Ar' and vicinal cis-Ar/OH steric interactions account for the results. The low enol or enediol content is mainly due to the relative stabilization of the aldehyde or acid form, and the β -Ar groups stabilize the enols mainly by conformation-dependent Ar-C:C conjugation and π (Ar)···HO H-bonding.

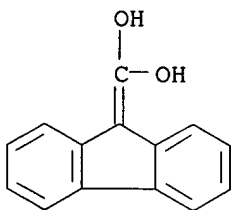
IT 263709-40-6

RL: PRP (Properties)

(ab initio study of relative stability of enols of carboxylic acids and aldehydes)

RN 263709-40-6 CAPLUS

CN Methanediol, 9H-fluoren-9-ylidene- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 62 THERE ARE 62 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 2 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2000:74486 CAPLUS

DOCUMENT NUMBER: 132:278887
 TITLE: Simultaneous pH-rate profiles applied to the two step consecutive sequence $A \rightarrow B \rightarrow C$: a theoretical analysis and experimental verification
 AUTHOR(S): Andraos, John; Lathioor, Edward C.; Leigh, William J.
 CORPORATE SOURCE: Department of Chemistry, University of Toronto, Toronto, ON, M5S 3H6, Can.
 SOURCE: Perkin 2 (2000), (2), 365-373
 CODEN: PRKTFO
 PUBLISHER: Royal Society of Chemistry
 DOCUMENT TYPE: Journal
 LANGUAGE: English

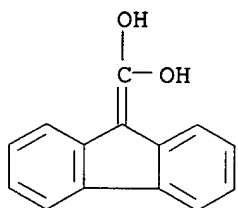
AB The absorbance extremum method introduced to resolve the rate constant-reaction step ambiguity problem in 2 step consecutive reactions is applied to cases where the rate constant in each step is pseudo 1st order and dependent on catalyst concentration. In particular, acid and base catalyzed reactions of substrates in aqueous solution are examined. Resultant simultaneous pH-rate profile functions are treated in the context of the ambiguity problem and a detailed account of the possible interactions between pH-rate profiles is also given. The merits of this method include its general scope, its applicability to reactions for which it may be exptl. difficult to resolve the ambiguity assignment by other means, its use of rate data acquired from original kinetic traces without requiring addnl. information. The theor. anal. is verified and tested exptl. for the hydration of fluorenylidene ketene in dilute aqueous HClO_4 solns.

IT 263709-40-6 263709-41-7

RL: FMU (Formation, unclassified); PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); FORM (Formation, nonpreparative); PROC (Process); RACT (Reactant or reagent) (mechanistic reaction intermediate; theor. anal. and exptl. verification of simultaneous pH-rate profiles applied to two step consecutive sequence $A \rightarrow B \rightarrow C$)

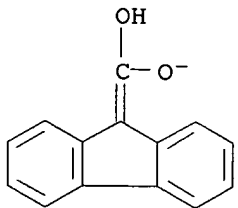
RN 263709-40-6 CAPLUS

CN Methanediol, 9H-fluoren-9-ylidene- (9CI) (CA INDEX NAME)



RN 263709-41-7 CAPLUS

CN Methanediol, 9H-fluoren-9-ylidene-, ion(1-) (9CI) (CA INDEX NAME)



REFERENCE COUNT: 17 THERE ARE 17 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 3 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1995:262850 CAPLUS

DOCUMENT NUMBER: 122:105122

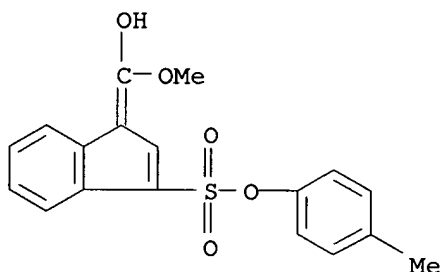
TITLE: Photodecomposition mechanism of o-diazonaphthoquinones studied by laser flash photolysis with infrared detection

AUTHOR(S): Oishi, Shigero; Watanabe, Yuriko; Kuriyama, Yasunao
 CORPORATE SOURCE: Sch. Sci., Kitasato Univ., Kitasato, Sagamihara, Kanagawa, 228, Japan
 SOURCE: Chemistry Letters (1994), (12), 2187-90
 CODEN: CMLTAG; ISSN: 0366-7022
 PUBLISHER: Nippon Kagakkai
 DOCUMENT TYPE: Journal
 LANGUAGE: English

AB Laser flash photolysis of an o-diazonaphthoquinone traced by monitoring IR in parallel with UV revealed the dynamic behavior of ketene intermediate, which appeared immediately after the laser pulse and changed swiftly to next intermediate. The fact that the conversion of ketene did not correspond to the formation of ketene hydrate suggested the existence of another intermediate between ketene and ketene hydrate.

IT **160815-99-6**
 RL: FMU (Formation, unclassified); PEP (Physical, engineering or chemical process); RCT (Reactant); FORM (Formation, nonpreparative); PROC (Process); RACT (Reactant or reagent)
 (mechanistic reaction intermediate; photodecompn. mechanism of o-diazonaphthoquinones studied by laser flash photolysis with IR detection)

RN 160815-99-6 CAPLUS
 CN 1H-Indene-3-sulfonic acid, 1-(hydroxymethoxymethylene)-, 4-methylphenyl ester (9CI) (CA INDEX NAME)



L18 ANSWER 4 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1995:40390 CAPLUS
 DOCUMENT NUMBER: 122:68048
 TITLE: Laser photolysis of naphthoquinone diazide in cyclohexane - two-laser chemistry
 AUTHOR(S): Bendig, J.; Mitzner, R.
 CORPORATE SOURCE: Inst. Organische Chemie, Humboldt-Univ., Berlin, D-10115, Germany
 SOURCE: Berichte der Bunsen-Gesellschaft (1994), 98(8), 1004-8
 CODEN: BBPCAX; ISSN: 0005-9021
 DOCUMENT TYPE: Journal
 LANGUAGE: English

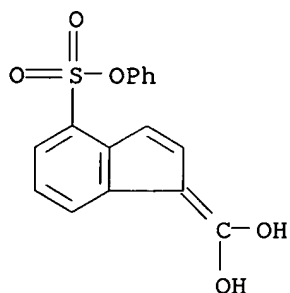
AB The laser photochem. of 1,2-naphthoquinone-diazide-(2)-5-sulfonic acid Ph ester in cyclohexane has been investigated. The photolysis expts. have been done using a KrF laser pulse (generation pulse) and a nitrogen laser pulse (transformation pulse) with various time delay from 40 ns up to 1 s. At a time delay between the two laser pulses in the μs-region, the formation of indene and cyclohexyl-indene derivs. has been observed, addnl. to the corresponding indenecarboxylic acid. The laser specific formation of these compds. is the result of the electronic excitation of the intermediately formed ketene and its reaction by decarbonylation. The time delay for getting a high yield of the indene and the cyclohexyl-indene derivs. correlates closely with the rise time and the life time of the ketene.

IT **145074-72-2**
 RL: FMU (Formation, unclassified); RCT (Reactant); FORM (Formation, nonpreparative); RACT (Reactant or reagent)

(transient; formation and photoreactions of transients in two-laser photolysis of naphthoquinone diazide in cyclohexane)

RN 145074-72-2 CAPLUS

CN 1H-Indene-4-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI)
(CA INDEX NAME)



L18 ANSWER 5 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1994:190791 CAPLUS

DOCUMENT NUMBER: 120:190791

TITLE: Kinetics and Mechanism of the Isomerization of
1H-Indene-1-carboxylic Acid to 1H-Indene-3-carboxylic
Acid in Aqueous Solution and Determination of Their
Keto-Enol Equilibrium Constants and Acid Dissociation
Constants of the Keto and Enol Forms. Implication for
the Photolysis of Diazonaphthoquinones

AUTHOR(S): Andraos, J.; Kresge, A. J.; Popik, V. V.

CORPORATE SOURCE: Department of Chemistry, University of Toronto,
Toronto, ON, M5S 1A1, Can.

SOURCE: Journal of the American Chemical Society (1994
) , 116(3), 961-7

CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE: Journal

LANGUAGE: English

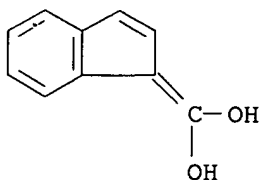
AB Rates of isomerization of 1H-indene-1-carboxylic acid to
1H-indene-3-carboxylic acid were measured in dilute aqueous solns. of HClO₄,
NaOH, and CH₃CO₂H and H₂PO₄⁻, (CH₃)₃CPH₃⁺, and HCO₃⁻ buffers. This gave
a rate profile which, together with the occurrence of general base
catalysis and sizable primary kinetic isotope effects, indicates that the
isomerization takes place through an enolization-reketonization reaction
sequence. The equilibrium constant of the isomerization reaction is K =
[indene-3-carboxylic acid]/[indene-1-carboxylic acid] = 200 in aqueous acid
solution and K = 100 in base. The ratio of products formed by ketonization
of the indenecarboxylic acid enol intermediate generated in the photolysis
of 2-diazo-1(2H)-naphthalenone is R = [indene-3-carboxylic
acid]/[indene-1-carboxylic acid] = 0.47 in aqueous acid solution and R = 20 in
base. The failure of previous investigations of the photolysis reaction
to detect any indene-1-carboxylic acid as the product is attributed to the
facile isomerization of this substance to indene-3-carboxylic acid and the
preponderance of the latter at equilibrium. The enol intermediate of this
isomerization reaction was also generated by flash photolysis of
2-diazo-1(2H)-naphthalenone and rates of its ketonization were measured in
dilute aqueous HClO₄ solns. Anal. of the data gave the enol acidity constant pK_{aE}
= 2.09. The results, in combination with those for the isomerization
reaction, also provided carbon acid acidity consts. (K_{aK}) and keto-enol
equilibrium consts. (K_E) for the two acids: pK_{aK} = 9.35 and pK_E = 7.26 for
indene-1-carboxylic acid and pK_{aK} = 11.69 and pK_E = 9.60 for
indene-3-carboxylic acid.

IT 153470-52-1P

RL: RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
(formation and tautomerization of)

RN 153470-52-1 CAPLUS

CN Methanediol, 1H-inden-1-ylidene- (9CI) (CA INDEX NAME)



L18 ANSWER 6 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1994:163330 CAPLUS

DOCUMENT NUMBER: 120:163330

TITLE: Flash Photolysis of α -Diazonaphthoquinones in Aqueous Solution: Determination of Rates and Equilibria for Keto-Enol Tautomerization of 1-Indene-3-carboxylic Acid

AUTHOR(S): Almstead, Ji In Kim; Urwyler, Bernhard; Wirz, Jakob
CORPORATE SOURCE: Institut fuer Physikalische Chemie, Universitaet Basel, Basel, CH-4056, Switz.

SOURCE: Journal of the American Chemical Society (1994), 116(3), 954-60

CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE: Journal

LANGUAGE: English

AB Flash photolysis of either 1-diazo-2(1H)-naphthalenone (1a) or 2-diazo-1(2H)-naphthalenone (1b) generates benzofulven-8-one (2). Hydrolysis of ketene 2 forms benzofulvene-8,8-diol (3), the enol tautomer of indene-3-carboxylic acid (4). PH rate profiles for the reactions $2 \rightarrow 3$ and $3 \rightarrow 4$ were determined in aqueous solution. Ketonization of 3 is catalyzed by acid and by base. Catalysis by protons sats. in strongly acidic solns., thereby defining the first ionization constant of the enol, $pK_{Ea} = 1.90 \pm 0.05$, catalysis by hydroxyl ions sats. in dilute base, defining the second ionization constant, $pK'_{Ea} = 8.3 \pm 0.2$. The first (OH) and second (CH) ionization consts. of 4 were determined by spectrophotometric titration, $pK_a = 4.50 \pm 0.03$ and $pK'_{Ka} = 15.2 \pm 0.2$. Two independent ests. of the enolization consts. of 4 and 4-, the first based on thermodyn. cycles, the second on the ratio of enolization and ketonization rates, were combined to give $pK_E = 9.3 \pm 0.3$, $pK'E = 6.6 \pm 0.3$. Ketene 2 is formed by irradiation of 1-bromo-2-naphthol at 12 K in an argon matrix, but neither it nor its isomer 2-bromo-1-naphthol were suitable for the generation and observation of 2 and 3 by flash photolysis in aqueous solution

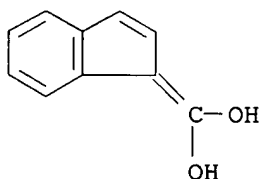
IT 153470-52-1 153470-53-2 153470-55-4

RL: PRP (Properties)

(ionization consts. and tautomerization of indenecarboxylic acid)

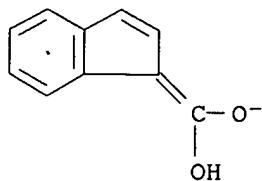
RN 153470-52-1 CAPLUS

CN Methanediol, 1H-inden-1-ylidene- (9CI) (CA INDEX NAME)

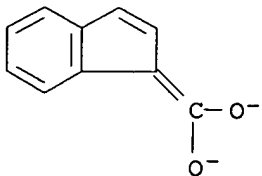


RN 153470-53-2 CAPLUS

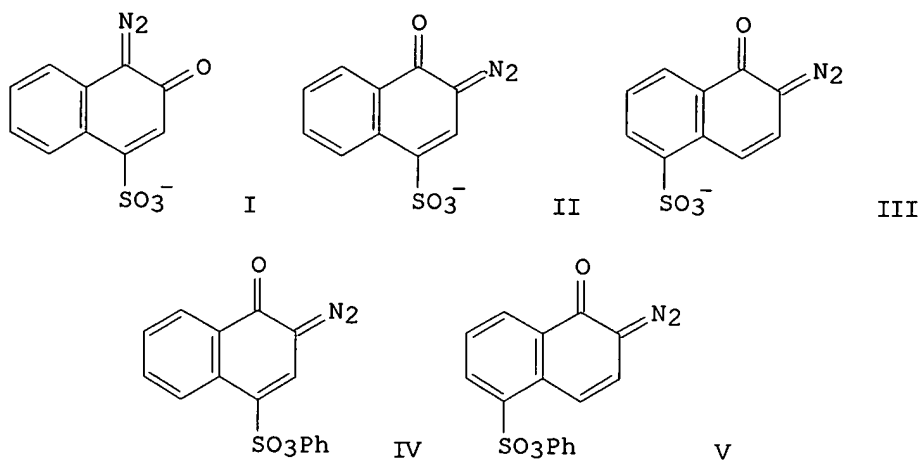
CN Methanediol, 1H-inden-1-ylidene-, ion(1-) (9CI) (CA INDEX NAME)



RN 153470-55-4 CAPLUS
 CN Methanediol, 1H-inden-1-ylidene-, ion(2-) (9CI) (CA INDEX NAME)



L18 ANSWER 7 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1994:76751 CAPLUS
 DOCUMENT NUMBER: 120:76751
 TITLE: Flash photolytic generation and study of ketene and carboxylic acid enol intermediates formed by the photolysis of diazonaphthoquinones in aqueous solution
 AUTHOR(S): Andraos, J.; Chiang, Y.; Huang, C. G.; Kresge, A. J.; Scaiano, J. C.
 CORPORATE SOURCE: Dep. Chem., Univ. Ottawa, Ottawa, ON, K1N 6N5, Can.
 SOURCE: Journal of the American Chemical Society (1993), 115(23), 10605-10
 CODEN: JACSAT; ISSN: 0002-7863
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 GI



AB Flash photolysis of each of five diazonaphthoquinones (1-diazo-2(1H)-oxonaphthalene-4-sulfonate (I), 2-diazo-1(2H)-oxonaphthalene-4-sulfonate (II), 2-diazo-1(2H)-oxonaphthalene-5-sulfonate (III), Ph 2-diazo-1(2H)-oxonaphthalene-4-sulfonate (IV), and Ph 2-diazo-1(2H)-oxonaphthalene-5-sulfonate (V) in aqueous solution was found to produce two short-lived intermediates preceding the ultimate indenecarboxylic acid reaction products. Decay of the first of these intermediates is catalyzed weakly by hydroxide ion but not by dilute perchloric acid nor by acetic acid

buffers, and its uncatalyzed reaction shows only weak solvent isotope effects; this serves to identify this intermediate as the ketene formed by photo-Wolff rearrangement of the diazonaphthoquinone. Decay of the second intermediate is catalyzed by perchloric acid in dilute acid solns., with saturation of this catalysis occurring in more concentrated acid, and it shows general acid catalysis in acetic acid buffers. The perchloric acid catalyzed reaction gives an appreciable solvent isotope effect in the normal direction ($k_H/k_D > 1$), which increases in magnitude as this catalysis becomes saturated. This serves to identify this intermediate as the indenecarboxylic acid enol formed by hydration of the first intermediate. The form of acid catalysis by perchloric acid and the change in isotope effect indicates that this enol ketonizes through its enolate ion, with a shift of initial state from enol to enolate as the acidity of the medium is decreased; anal. of the kinetic data shows the enols to be rather strong acids, with $pK_a = 0.4-1.3$.

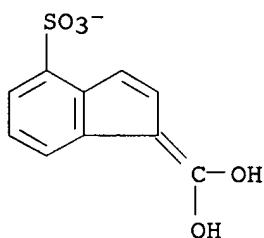
IT 116670-10-1 145074-71-1 145074-72-2
152339-95-2

RL: PRP (Properties)

(intermediate, photo-Wolff rearrangement of diazonaphthoquinones,
polymerization of)

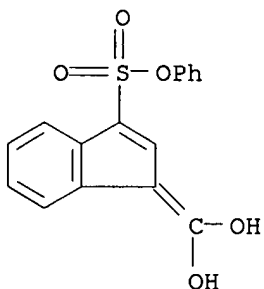
RN 116670-10-1 CAPLUS

CN 1H-Indene-4-sulfonic acid, 1-(dihydroxymethylene)-, ion(1-) (9CI) (CA
INDEX NAME)



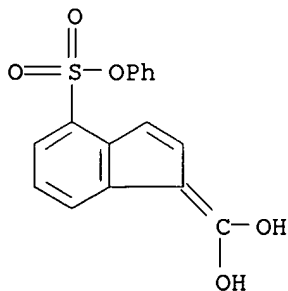
RN 145074-71-1 CAPLUS

CN 1H-Indene-3-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI)
(CA INDEX NAME)

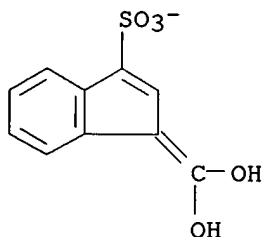


RN 145074-72-2 CAPLUS

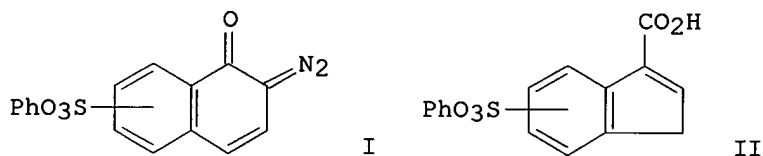
CN 1H-Indene-4-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI)
(CA INDEX NAME)



RN 152339-95-2 CAPLUS
CN 1H-Indene-3-sulfonic acid, 1-(dihydroxymethylene)-, ion(1-) (9CI) (CA INDEX NAME)



L18 ANSWER 8 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1993:38553 CAPLUS
DOCUMENT NUMBER: 118:38553
TITLE: Synthesis and photochemistry of 1,2-naphthoquinonediazide-(2)-n-sulfonic acid derivatives
AUTHOR(S): Bendig, J.; Sauer, E.; Polz, K.; Schopf, G.
CORPORATE SOURCE: Inst. Org. Chem., Humboldt Univ., Berlin, 0-1040, Germany
SOURCE: Tetrahedron (1992), 48(42), 9207-16
CODEN: TETRAB; ISSN: 0040-4020
DOCUMENT TYPE: Journal
LANGUAGE: English
GI



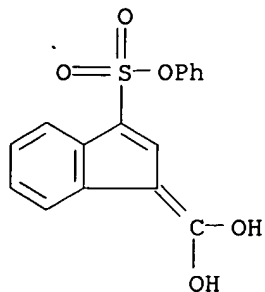
AB The 1,2-naphthoquinonediazide-(2)-6- and -7-sulfonic acid esters I (sulfonyl position = 7, 8) were synthesized for the first time starting from the corresponding 1-naphthylamine-6- and -7-sulfonic acids, resp., via Bucherer reaction, nitrosation, reduction, diazotation, sulfochlorination, esterification. The synthesis of the corresponding 8-sulfonic acid ester was not successful by this way. On photolysis, I form the corresponding (phenoxysulfonyl)indenecarboxylic acids II in the same manner like the known 5-sulfonic acid derivative. On the other hand, photolysis of the 4-sulfonic acid ester photochem. induced ester cleavage occurs addnl. ($\lambda < 320$ nm).

IT 145074-71-1P 145074-72-2P 145074-73-3P
145074-74-4P

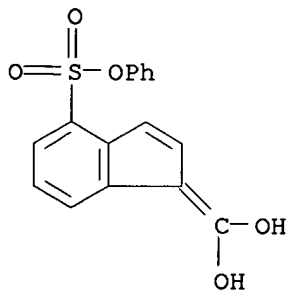
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and rearrangement of)

RN 145074-71-1 CAPLUS

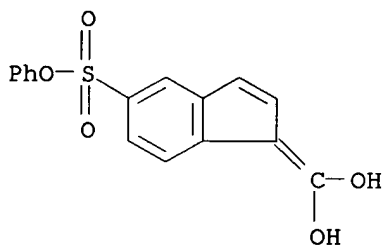
CN 1H-Indene-3-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI)
(CA INDEX NAME)



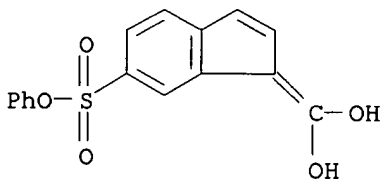
RN 145074-72-2 CAPLUS
 CN 1H-Indene-4-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI)
 (CA INDEX NAME)



RN 145074-73-3 CAPLUS
 CN 1H-Indene-5-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI)
 (CA INDEX NAME)



RN 145074-74-4 CAPLUS
 CN 1H-Indene-6-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI)
 (CA INDEX NAME)



L18 ANSWER 9 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1989:621868 CAPLUS
 DOCUMENT NUMBER: 111:221868
 TITLE: Photochemical reactions of 1-oxo-2-diazo-1,2-dihydronaphthalenes and reactivity of their products
 AUTHOR(S): Tanigaki, K.; Honda, T.; Ebbesen, T. W.
 CORPORATE SOURCE: Fundam. Res. Lab., NEC Corp., Kawasaki, 213, Japan
 SOURCE: Polymeric Materials Science and Engineering (

DOCUMENT TYPE:

Journal

LANGUAGE:

English

AB Photochem. reactions of 4-tolyl 1-oxo-2-diazo-1,2-dihydronaphthalene-5-sulfonate (DNQ-5STL) were studied as a typical example of 6-membered ring α -diazoketones, together with its 2 prototype mols., i.e., 1-oxo-2-diazo-1,2-dihydrobenzene and 1-oxo-2-diazo-1,2-dihydronaphthalene, by reverse-phase liquid chromatog. The obtained products under different reaction conditions, such as photochem. reactions of pure solid DNQ-5STL in air and in vacuo, were examined. The reactivity of the carboxy compds. produced in air or in a H₂O-containing solution is discussed. They exhibit decarboxylation, dimerization or azo formation in the presence of bases, being markedly dependent on the type of mols. The azo formation rate constant of the 3-carboxyindene analog from DNQ-5STL is much greater than that of its dimerization.

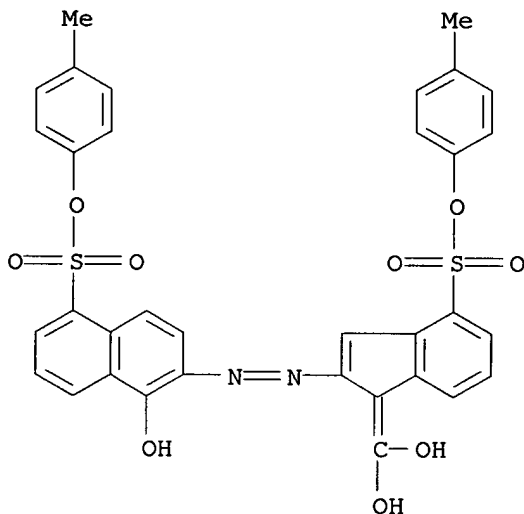
IT 123658-18-4P

RL: FORM (Formation, nonpreparative); PREP (Preparation)

(formation of, in reaction of photoproduct from photochem. reaction of tolyl oxodiazodihydronaphthalenesulfonate)

RN 123658-18-4 CAPLUS

CN 1-Naphthalenesulfonic acid, 6-[[1-(dihydroxymethylene)-4-[(4-methylphenoxy)sulfonyl]-1H-inden-2-yl]azo]-5-hydroxy-, 4-methylphenyl ester (9CI) (CA INDEX NAME)



L18 ANSWER 10 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1988:601125 CAPLUS

DOCUMENT NUMBER: 109:201125

TITLE: Mechanism of photochemical conversion of 1,2-naphthoquinonediazides in solution

AUTHOR(S): Shibata, Tsuyoshi; Koseki, Kenichi; Yamaoka, Tsuguo; Yoshizawa, Masayuki; Uchiki, Hisao; Kobayashi, Takayoshi

CORPORATE SOURCE: Fac. Eng., Chiba Univ., Chiba, 260, Japan

SOURCE: Journal of Physical Chemistry (1988), 92(22), 6269-72

CODEN: JPCHAX; ISSN: 0022-3654

DOCUMENT TYPE:

Journal

LANGUAGE:

English

AB The photochem. conversion of 1,2-naphthoquinonediazide-5-sulfonic acid (NQDS) in solution was studied by nanosec time-resolved spectroscopy, and the observed transient absorption was assigned to the intermediate produced by the photodecompn. of NQDS. The intermediate was formed by the hydration of photochem. generated ketene. The formation rate constant of ketene hydrate in the mixed solvent of 1,4-dioxane/H₂O increased with the H₂O

concentration The conversion process from the ketene hydrate to 3-indenecarboxylic acid in aqueous solution is the acid-catalyzed reaction with a rate constant of $5.2 + 102 \text{ s}^{-1} + 2.8 + 107 [\text{H}^+] \text{ M}^{-1} \text{ s}^{-1}$, being H^+ ion concentration

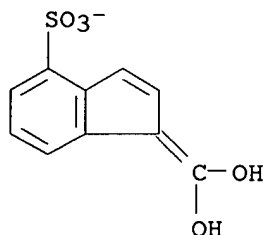
IT **116670-10-1P**

RL: FORM (Formation, nonpreparative); PREP (Preparation)

(formation of, in photolysis of naphthoquinonediazidesulfonate in aqueous solns.)

RN 116670-10-1 CAPLUS

CN 1H-Indene-4-sulfonic acid, 1-(dihydroxymethylene)-, ion(1-) (9CI) (CA INDEX NAME)



L18 ANSWER 11 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1988:437562 CAPLUS

DOCUMENT NUMBER: 109:37562

TITLE: Electrophilic substitution of benzofulvenes with activated sulfoxides

AUTHOR(S): Teuber, Dorothee; Hartke, Klaus

CORPORATE SOURCE: Inst. Pharm. Chem., Univ. Marburg, Marburg, D-3550, Fed. Rep. Ger.

SOURCE: Liebigs Annalen der Chemie (1988), (1), 39-42

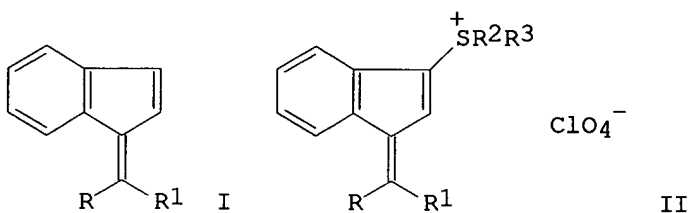
CODEN: LACHDL; ISSN: 0170-2041

DOCUMENT TYPE: Journal

LANGUAGE: German

OTHER SOURCE(S): CASREACT 109:37562

GI



AB The benzofulvenes I ($\text{R} = \text{R}_1 = \text{Ph}, \text{Me}, \text{EtO}, \text{MeS}$; $\text{R} = \text{Me}, \text{R}_1 = \text{Ph}$) were treated with $\text{R}_2\text{R}_3\text{SO}$ [$\text{R}_2 = \text{R}_3 = \text{Me}, \text{PhCH}_2, \text{Ph}, \text{p-MeC}_6\text{H}_4$; $\text{R}_2 = \text{R}_3 = (\text{CH}_2)_4, \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$] in presence of $(\text{F}_3\text{CCO})_2\text{O}$ followed by aqueous LiClO_4 to give the sulfoniobenzofulvene perchlorates II.

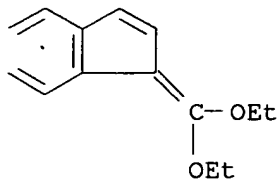
IT **115176-68-6P**

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and reaction with sulfoxides)

RN 115176-68-6 CAPLUS

CN 1H-Indene, 1-(diethoxymethylene)- (9CI) (CA INDEX NAME)



IT 115176-52-8P 115176-54-0P

RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

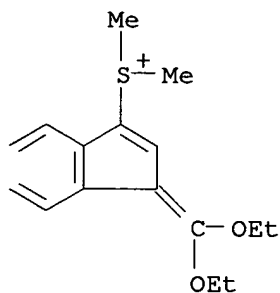
RN 115176-52-8 CAPLUS

CN Sulfonium, [1-(diethoxymethylene)-1H-inden-3-yl]dimethyl-, perchlorate
(9CI) (CA INDEX NAME)

CM 1

CRN 115176-51-7

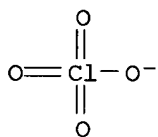
CMF C16 H21 O2 S



CM 2

CRN 14797-73-0

CMF C1 O4



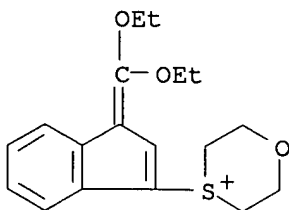
RN 115176-54-0 CAPLUS

CN 1,4-Oxathianium, 4-[1-(diethoxymethylene)-1H-inden-3-yl]-, perchlorate
(9CI) (CA INDEX NAME)

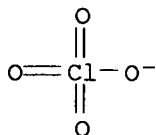
CM 1

CRN 115176-53-9

CMF C18 H23 O3 S



CRN 14797-73-0
CMF Cl 04



L18 ANSWER 12 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1987:597239 CAPLUS

DOCUMENT NUMBER: 107:197239

TITLE: Nucleophilic attacks on carbon-carbon double bonds.
34. Intramolecular elements effect in competitive
expulsion of two halide nucleofuges as a tool for
investigating the rapid step of nucleophilic vinylic
substitution

AUTHOR(S): Avramovitch, Bianca; Weyerstahl, Peter; Rappoport, Zvi
CORPORATE SOURCE: Dep. Org. Chem., Hebrew Univ., Jerusalem, 91904,
Israel

SOURCE: Journal of the American Chemical Society (1987
, 109(22), 6687-97
CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE: Journal

LANGUAGE: English

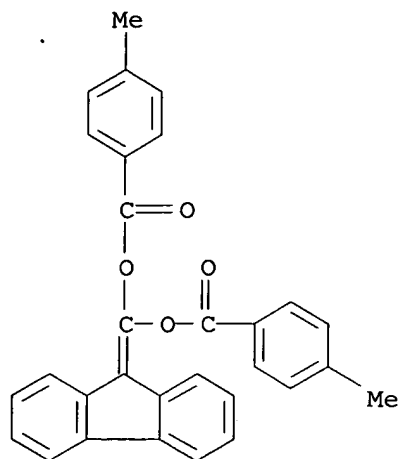
AB Substitution of 9-(bromochloromethylene)fluorene (I) and
(p-O₂NC₆H₄)₂C:CClBr (II) with p-MeC₆H₄S⁻ and p-MeC₆H₄O⁻ ions gives the
monobromo, monochloro, and disubstitution products. The
[monochloro]/[monobromo] substitution product ratios were determined in CD₃CN,
DMSO-d₆, and DMSO-d₆-CD₃OD under conditions where disubstitution was
negligible. The ratios were 2.0-3.2, were slightly higher for I than for
II, and showed no discernible solvent dependence. The ratios did not
change in the presence of radical traps, although an ESR spectrum was
observed with I and p-MeC₆H₄S⁻. The intermol. element effects kBr/kCl,
derived from competitive substitution of I or II with their dibromo or
dichloro analogs, were 1.2-1.76. The results were interpreted in terms of
a multistep nucleophilic vinylic substitution via an intermediate
carbanion, which may be formed either directly or by an initial
single-electron transfer followed by combination of the anion radical with
the radical. The product ratios were thus identified as the ratios of the
rate consts. for Br⁻ and Cl⁻ expulsion [kel(Br)/kel(Cl) - the intramol.
element effect] from the carbanion. The low ratios and their relative
insensitivity to the solvent and to the delocalizing ability of neg.
charge of the β-substituents were ascribed to an early transition
state for halide-ion expulsion from the carbanion. Generalizations
concerning the expulsion of poor and good nucleofuges from carbanions
substituted by poor and good electron-withdrawing groups were discussed.

IT 110223-43-3P

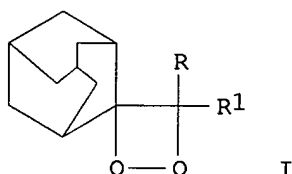
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 110223-43-3 CAPLUS

CN Benzoic acid, 4-methyl-, 9H-fluoren-9-ylidene[(4-methylbenzoyl)oxy]methyl
ester (9CI) (CA INDEX NAME)



L18 ANSWER 13 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1983:160065 CAPLUS
 DOCUMENT NUMBER: 98:160065
 TITLE: Thermal stability of spiro[adamantane-[1,2]dioxetanes]
 AUTHOR(S): Adam, Waldemar; Encarnacion, Luis A. Arias; Zinner, Klaus
 CORPORATE SOURCE: Inst. Org. Chem., Univ. Wuerzburg, Wuerzburg, D-8700, Fed. Rep. Ger.
 SOURCE: Chemische Berichte (1983), 116(3), 839-46
 CODEN: CHBEAM; ISSN: 0009-2940
 DOCUMENT TYPE: Journal
 LANGUAGE: English
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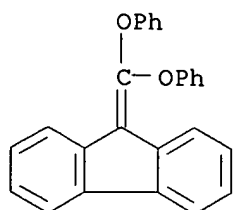


AB Activation parameters were determined for the thermolysis of I (R, R1 = Me, CH2Br; OPh, OPh; H, OCH2Ph; H, OC6H4Br-4; H, OPh) and some related 1,2-dioxetanes by a chemiluminescence method. The stabilization of I cannot be interpreted by inertial mass, torsional, or compression arguments. A transoid biradical, in which the participating orbitals are antiperiplanar, promotes C-C cleavage, but the bulky adamantane moiety hinders formation of this species from the initially formed cisoid biradical.

IT **85374-62-5**
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with dibromodimethylhydantoin and hydrogen peroxide)

RN 85374-62-5 CAPLUS

CN 9H-Fluorene, 9-(diphenoxymethylene)- (9CI) (CA INDEX NAME)



ACCESSION NUMBER: 1977:55122 CAPLUS

DOCUMENT NUMBER: 86:55122

TITLE: Cyclic peroxides. 44. A convenient and efficient preparation of aromatic α -hydroperoxy acids via oxygenation of α -lithio enolates, prepared by direct α -lithiation of arylacetic acids

AUTHOR(S): Adam, Waldemar; Cueto, Omar

CORPORATE SOURCE: Dep. Chem., Univ. Puerto Rico, Rio Piedras, P. R.

SOURCE: Journal of Organic Chemistry (1977), 42(1), 38-40

CODEN: JOCEAH; ISSN: 0022-3263

DOCUMENT TYPE: Journal

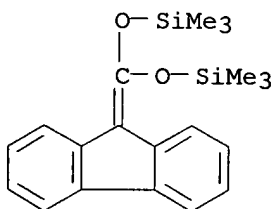
LANGUAGE: English

AB Arylacetic acids were α -lithiated by treatment with BuLi in THF at -40° . The efficiency of the lithiation was shown by treatment of the α -lithiocarboxylic acids with electrophiles, i.e., D₂O, Ph₂CO, Me₃SiCl, and O. In the last case, inverse addition at dry ice temperature gave the α -hydroperoxy acids corresponding to PhCH₂CO₂H, Ph₂CHCO₂H, and 9-fluorene-carboxylic acid.

IT 40348-09-2P

RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 40348-09-2 CAPLUS

CN 3,5-Dioxa-2,6-disilaheptane, 4-(9H-fluoren-9-ylidene)-2,2,6,6-tetramethyl-
(9CI) (CA INDEX NAME)

ACCESSION NUMBER: 1973:58504 CAPLUS

DOCUMENT NUMBER: 78:58504

TITLE: Ketene alkyltrialkylsilyl acetals. Synthesis, pyrolysis, and NMR studies

AUTHOR(S): Ainsworth, C.; Chen, Francis; Kuo, Yu-Neng

CORPORATE SOURCE: Dep. Chem., Colorado State Univ., Fort Collins, CO, USA

SOURCE: Journal of Organometallic Chemistry (1972), 46(1), 59-71

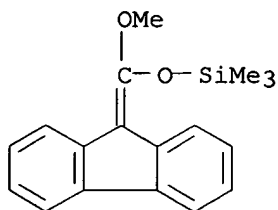
CODEN: JORCAI; ISSN: 0022-328X

DOCUMENT TYPE: Journal

LANGUAGE: English

AB Ketene alkyltrialkylsilyl acetals RR1C:C(OMe)OSiMe₃ (I) were prepared by reaction of disubstituted malonates and sodium-xylene, or by reaction of the α -anion of substituted acetates with Me₃SiCl. Carbomethoxyketene methyltrimethylsilyl acetals Me₂O₂CRC:C(OMe)OSiMe₃ (II) were also prepared. Pyrolysis of diaryl I gave diaryl ketenes in good yield; the mechanism has been established as intramolecular, employing 180°. Alkyl, aryl and dialkyl I on pyrolysis gave ketene-ketene acetal addition compounds. RR1C:C(OSiMe₃)(CRR1CO₂Me (III). Spectral studies of I are consistent with a dipolar structure Ar₂C=C⁺(OMe)OSiMe₃. Freedom of rotation about a carbon-carbon double bond is determined by the substituents. Spectral studies support fluxional behavior in II in which the carbomethoxy and trimethylsilyloxy groups are cis. The results of mass fragmentation of I are similar to their thermolytic cleavage. Interestingly, however, III in the mass spectrometer are fragmented into the ketene and ketene acetal fragments from which molecules they are thermally formed.

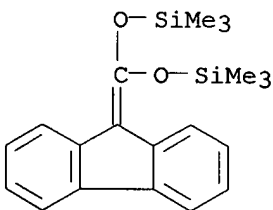
IT 40195-33-3
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (preparation pyrolysis and NMR of)
 RN 40195-33-3 CAPLUS
 CN Silane, (9H-fluoren-9-ylidenemethoxymethoxy)trimethyl- (9CI) (CA INDEX NAME)



L18 ANSWER 16 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1973:43575 CAPLUS
 DOCUMENT NUMBER: 78:43575
 TITLE: Ketene bis(trialkylsilyl) acetals. Synthesis, pyrolysis, and spectral studies
 AUTHOR(S): Ainsworth, C.; Kuo, Yu-Neng
 CORPORATE SOURCE: Dep. Chem., Colorado State Univ., Fort Collins, CO, USA
 SOURCE: Journal of Organometallic Chemistry (1972), 46(1), 73-87
 CODEN: JORCAI; ISSN: 0022-328X
 DOCUMENT TYPE: Journal
 LANGUAGE: English

AB Two high yield synthetic methods are described for the preparation of alkyl, dialkyl, aryl and diaryl ketene bis(trialkylsilyl) acetals. One is by reaction of α -metalated trimethylsilyl carboxylates with Me₃SiCl and the other is by interaction of dianions of carboxylic acids and Me₃SiCl. The dianion of cyclopropane carboxylic acid and Me₃SiCl gave C-silylated ester in 90% yield. Pyrolysis of diphenyl ketene bis(trialkylsilyl) acetals to diphenyl ketene and bis(trialkylsilyl) ethers was shown by crossover expts. to proceed intermol. pyrolysis of monosubstituted and dialkyl ketene bis(trimethylsilyl) acetals gave ketene-ketene acetal addition products (III) which on solvolysis afforded β -keto acids in high yield.

IT 40348-09-2
 RL: PRP (Properties)
 (spectrum of)
 RN 40348-09-2 CAPLUS
 CN 3,5-Dioxa-2,6-disilaheptane, 4-(9H-fluoren-9-ylidene)-2,2,6,6-tetramethyl- (9CI) (CA INDEX NAME)



L18 ANSWER 17 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1966:465536 CAPLUS
 DOCUMENT NUMBER: 65:65536
 ORIGINAL REFERENCE NO.: 65:12207d-h,12208a-h,12209a-b
 TITLE: Carbocyclic substituted piperidylidioxolanes
 INVENTOR(S): Hardie, Waldo R.; Halverstadt, Isaac F.
 PATENT ASSIGNEE(S): Cutter Laboratories, Inc.

SOURCE: 15 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3262938		19660726	US	19610210 <--
PRIORITY APPLN. INFO.:			US	19610210

GI For diagram(s), see printed CA Issue.

AB The title compds. were prepared by the condensation of a ketone or ketal with a piperidyl vicinal glycol in the presence of HCl. The ketals were prepared by two methods: Method A, exchange between the appropriate ketone and 2,2-dimethoxypropane, and Method B, treatment of the ketone first with PCl5 then with NaOMe to form the dimethoxy derivative. The tabulated R1R2C(OR)2 were prepared 2-Pyridyl-1,2-ethanediol-HCl was hydrogenated in H2O over PtO2 to give a mixture of 2 racemates of 2-piperidyl-1,2-ethanediol (I) HCl salt. Method, R1, R2, R, B.p./mm., n25D; A, Me, Ph, Bu, 75°/3, 1.4747; A, Et, Ph, Bu, 89-90°/3, 1.4767; A, PhCH2, Bu, 147-54°/3, 1.5623; A, Ph, Ph, Me, m. 107-8°, -; A, Me, Ph2CH, Bu, 132-5°/1, 1.5620; A, Ph, PhCH2, Bu, 144-6°/3, -; B, 4-MeOC5H4, 4-MeOC6H4, Bu, 170-2°/1, 1.5302; B, 2-thienyl, Ph, Me, m. 56-9°, -; B, Ph, 4-ClC5H4, Me, 128°/1, 1.5667; B, 4-ClC6H4 4-ClC6H4, Me, m. 68.5-70°, -; B, fluoren-9-ylidene, Me, m. 86.7.5°, -; An alc. solution of this mixture was treated with NaOMe in MeOH to give the free bases which were dissolved in Et2O. The solution yielded the β racemate of I, m. 99-101°. After concentration, the mother liquors yielded the α -racemate of I, m. 77-8°. Acidic hydrolysis with HCl of 2,2-diphenyl-4-(2-piperidyl)-1,3-dioxolane (II) HCl salt α -racemate yielded I.HCl α -racemate, m. 100-1°, and hydrolysis of II.HCl β -racemate gave I.HCl β -racemate, m. 139-41°. Method C: I.HCl (86 g.), 103 g. (MeO)2CPh2, and 20 ml. iso-PrOH was heated at 130° with stirring. Dry HCl was passed in below the surface until the mixture was strongly acidic and the mixture was refluxed 8 hrs. with slow distillation of solvent which was replaced as needed. Removal of solvent followed by washing with Et2O and crystallization of the residue from EtOH then MeOHEt2O yielded 54.5 g. II.HCl, m. 248-52°. Extraction of the etherwashed residue from Method C with hot EtOH followed by filtration of the EtOH gave a residue, II.HCl β -racemate, m. 301°, and a solution which yielded II.HCl α -racemate, m. 256-60°. Method D: I.HCl (1436 g.) in 2 l. iso-PrOH was treated at 80° with 2012 g. (MeO)2CPH2 then with 1 g. dry HCl in iso-PrOH. The mixture was heated and stirred 2 hrs. to give 2042 g. crude II.HCl, m. 234-8°, containing approx. 60% α -racemate and 40% β -racemate of II.HCl. A II.HCl racemate mixture containing 15-20% β -racemate was converted to 76% DL-tartrate salt, m. 233-5°. II α -racemate DL-tartrate salt m. 222-8°. II.HCl α -racemate was also prepared directly from I α -racemate without isolation of the HCl salt. II.HCl α -racemate was converted to the free base then treated with L-(+)-tartaric acid to give (+)-II (+)-tartrate, m. 248-54° (decomposition). The mother liquors from this reaction were hydrolyzed to the free base then treated with D- (-)-tartaric acid to give (-)-II (-)-tartrate, m. 248-54° (decomposition). (+)-II (+)-tartrate was converted to the HCl salt, m. 248-54° (decomposition), α 20D 34° (c 2, MeOH). Similarly prepared was (-)-II.HCl, m. 248-54°, α 20D -34.5° (c 2, MeOH). I.HCl was condensed with EtCOPh in BuOH at 125° by Method C to give III (R1 = Et, R2 = Ph), m. 256-7°. Method E: I.HCl α -racemate (145.7 g.) and 209 g. EtC(OPr)2Ph in 900 ml. iso-PrOH was brought to pH 2 with anhydrous HCl gas then refluxed 1 hr. to give 175 g. III α -racemate (R1 = Et, R2 = Ph), m. 251.5-3°. After isolation of further α -racemate, the mother liquors were freed of α -racemate by successive formation of the free base, the DL-tartrate, the free base, and the HCl salt to give 2.4 g. of a γ -racemate of III.HCl (R1 = Et, R2 = Ph), m. 175-7°, solidified 195°, remelted at 241°. The following HI were prepared (method, starting racemate, R1, R2, and m.p.

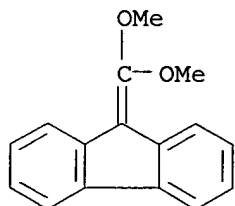
given): E, β , Et, Ph, 250-1°; D, mixture, H, Ph, 221°; E, β , Me, Ph, 241-3°; D, mixture, 4-ClC₆H₄, Ph, 265-7°; D (no solvent), mixture, 4-ClC₆H₄, 4-ClC₆H₄, 210-15°; E, α , 2-thienyl, Ph, 221-3°; E, β , 2-thienyl, Ph, 282°; E, α , 4-MeOC₆H₄, 4-MeOC₆H₄, 282-3°; D, mixture, PhCH₂, H, 163-5°; E, α , PhCH₂, Ph, 240-4°; C (on ketone), mixture, PhCH₂, PhCH₂, 183-6°; E, α , PhCH₂, PhCH₂, 184-5°; E, β , PhCH₂, PhCH₂, 245°; E, β , PhCH₂, Me, 205-10°; C (on ketone in BuOH), mixture, cyclohexyl, cyclohexyl, 243-5°; E, α , hexyl, hexyl (V), 153-5°; E, β , hexyl, hexyl (VI), 132-3°; E, α , octyl, octyl (VII), 105-12°; E, α , Bu, Bu (VIII), 160.5-62°. II β -racemate was hydrogenated at 60 psi. in glacial HOAc over Rh/Al₂O₃ to give III (R₁ = R₂ = cyclohexyl) β -racemate, m. 288°. II α -racemate with 37% aqueous HCHO was hydrogenated in MeOH over Pd/C to give IV (R = Me) α -racemate, m. 268-75°; methiodide m. 211-14°. Similarly prepared were: IV (R = Me) β -racemate, m. 183-5° (methiodide m. 237-8°); (+)-IV (R = Me), m. 275-87°, α 25D 31.8° (c 1 MeOH); (-)-IV (R = Me), m. 283-7°, α 24D -30.7° (c 1, MeOH). II.HCl α -racemate was converted to the free base then treated directly with EtCOCl in (CH₂Cl)₂ at 0-5° to give IV (R = EtCO) α -racemate, m. 92-3.5°. Similarly prepared were: IV (R = ClCH₂CO) α -racemate, m. 162.5-7.5°, its β -racemate, m. 153-4°, and IV (R = EtCO) β -racemate, m. 123-5°. Reduction of the latter with LiAlH₄ in Et₂O gave IV (R = Pr) β -racemate, m. 170-1.5°. Similarly prepared was IV (R = Pr) α -racemate, m. 201-2°. II α -racemate with PhCH₂Br in C₆H₆ gave IV (R = PhCH₂) α -racemate HCl salt, m. 172-4°. II β -racemate was refluxed 6 hrs. in absolute EtOH with PhCH₂Br to give IV (R = PhCH₂) β -racemate HCl salt, m. 212-15°. Similarly prepared were: (+)-IV (R = PhCH₂) HCl salt (from the α -racemate), m. 201.5-203°, α 25D 16.75° (c 2, MeOH); (-)-IV (R = PhCH₂) HCl salt (from the α -racemate), m. 205-6°, α 25D -16.62° (c 2, MeOH); (+)-IV (R = allyl) HCl salt (from the α -racemate), m. 198.5-9.5°, α 22D 9.0° (c 1, MeOH). II α -racemate was heated 6 hrs. in a pressure bottle at 100° with (CH₂)₂O and MeOH-H₂O 3:1 to give IV (R = HOCH₂CH₂) HCl salt α -racemate, m. 218-19.5°. IV (R = ClCH₂CO) β -racemate was refluxed 3 hrs. with Et₂NH in C₆H₆ to give IV (R = Et₂NCH₂CO) β -racemate, HCl salt m. 175-6°. Similarly prepared was the α -racemate, m. 182-3°. IV (R = Et₂NCH₂CO) β -racemate was reduced with LiAlH₄ in Et₂O to give IV (R = Et₂NCH₂CH₂) β -racemate HCl salt, m. 180°. 4-Pyridylmethanol (IX) (100 g.) and 28 g. paraformaldehyde in 100 ml. H₂O was treated with 2 ml. 10% NaOH, the mixture refluxed 20 hrs., then treated with 6N HCl to give a crystalline mixture of HCl salts of 4-pyridyl-1,2-ethanediol and IX. This mixture (122 g.) and 190 g. (MeO)₂CPh₂ in iso-PrOH and EtOH was acidified with HCl then refluxed 16 hrs. to give 27 g. 2,2-diphenyl-4-(4-pyridyl)-1,3-dioxolane-HCl (X), m. 211.514°. X was hydrogenated in EtOH. over PtO₂ at 60 psi. to give 2,2-diphenyl-4-(4-piperidyl)-1,3-dioxolane-HCl (XI), m. 209.1-11.7°. Reductive methylation of XI gave 4-(1-methyl-4-piperidyl)-2,2-diphenyl-1,3-dioxolane-HCl (XII), m. 234.5-36°. Dry HCl gas was admitted under the surface of a solution of I.HCl (39 g.) and 40 g. cyclohexanone in 150 ml. iso-PrOH. After several days the mixture yielded 9.2 g. 2-(2-piperidyl)-1,4-dioxaspiro[4.5]decane-HCl (XIII, R = H), m. 223°. Other XIII prepared were (R, m.p. given): 6-Me, 247-50°; 6-Et, 263°; 7-Me, 232-3°; 8-Me, 258°; 7,9-di-Me, 219-20°; 8-tert-Bu, 264-5°; 6-Cl, 235-7°; 8-Cl (α -racemate), 239° (decomposed); 8-Cl (β -racemate), 206-7°; 8-Me-8-Ph, 215-30° (left to react 6 weeks at room temperature then the oily product was kept 5 months to crystallize); 8-Me-8-Ph (α -racemate), 244-52°; 8-Me-8-Ph (β -racemate), 202-19°; 8,8-di-Ph (β -racemate), 277-85°. Similarly prepared also was 2-(2-piperidyl)-1,4-dioxaspiro[4.6]undecane-HCl, m. 220-3°. Condensation of 9,9-dimethoxyfluorene (XIV) and I.HCl by Method D gave 4-(2-piperidyl)spiro(1,3-dioxolane 2,9'-fluorene) HCl salt (XV), decomposed

275°. Condensation of XIV with I α -racemate HCl salt by Method E gave XV α -racemate, m. 284-5°. Similarly prepared was XV β -racemate, m. 258-9°. IV (R = Me) β -racemate HCl salt was converted to the free base then to the N-oxide with H₂O₂ in MeOH; the HCl salt decomposed 200°. Similarly prepared were IV (R = Me) α -racemate N-oxide HCl salt, Me₂CO solvate, m. 113°; and IV (R = PhCH₂) α -racemate N-oxide HCl salt, m. 191° (decomposition). Reductive methylation of V gave 2,2-diethyl-4-(1-methyl-2-piperidyl)-1,3-dioxolane-HCl α -racemate (XVI), m. 106°; methiodide m. 113-16°. The title compds. have antispasmodic and local anesthetic activity. (+)II is a central nervous depressant. V-VIII, XI, XII, and XVI have anti-pancreatic lipase activity.

IT **6861-54-7**, Fluorene, 9-carbonyl-, dimethyl acetal (preparation of)

RN 6861-54-7 CAPLUS

CN Fluorene, 9-carbonyl-, dimethyl acetal (7CI, 8CI) (CA INDEX NAME)



L18 ANSWER 18 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1966:412000 CAPLUS

DOCUMENT NUMBER: 65:12000

ORIGINAL REFERENCE NO.: 65:2164f-g

TITLE: Acylation of aromatic hydrocarbons

AUTHOR(S): Shamis, E. M.; Dashevskii, M. M.

CORPORATE SOURCE: Polytech. Inst., Odessa

SOURCE: Zhurnal Obshchei Khimii (1966), 2(2), 280-2
CODEN: ZOKHA4; ISSN: 0044-460X

DOCUMENT TYPE: Journal

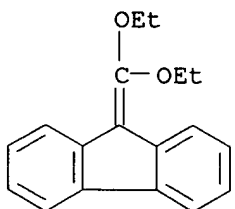
LANGUAGE: Russian

AB Aromatic substrates (0.1-0.2 mole) heated with RCOCl or PhSO₂Cl (0.1 mole) in the presence of .apprx.0.3 + 10⁻³ mole AlCl₃ 6-10 hrs. at 140-50° (200° in some cases) gave the following acylated products in up to 92% yields: 2,4-Me₂C₆H₃Bz, b₉ 178-81°; 2,4-isomer, b₁₀ 161°; 2,4-isomer, b. 320°; 2,4-Me₂C₆H₃SO₂Ph, m. 81-2°; p-BzC₆H₄OPh, m. 68°; p-MeOC₆H₄Bz, b₈ 180°, m. 61°; pMeOC₆H₄COAm, b₈ 156°, m. 41°; p-MeOC₆H₄COPr, b. 270-80°; Ph₂SO₂, m. 123°; p-MeC₆H₄Bz, m. 58°; mixed 1- and 2-C₁₀H₇COPh, b₈ 225°; p-BzC₆H₄Ph, b₉ 245°. Reactions with ZnCl₂ were best for the more reactive aromatic substrates such as xylene, C₁₀H₈, Ph₂, and MePh; AlBr₃ gave poorer yields than AlCl₃.

IT **6397-78-0**, Fluorene, 9-(diethoxymethylene)- (preparation of)

RN 6397-78-0 CAPLUS

CN 9H-Fluorene, 9-(diethoxymethylene)- (9CI) (CA INDEX NAME)



L18 ANSWER 19 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN

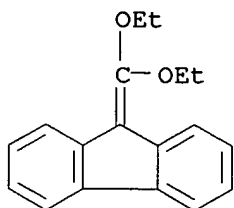
ACCESSION NUMBER: 1966:411999 CAPLUS
DOCUMENT NUMBER: 65:11999
ORIGINAL REFERENCE NO.: 65:2164e-f
TITLE: Synthesis of acetals by reaction of diazoalkanes with
tert-butyl hypochlorite
AUTHOR(S): Baganz, H.; May, H. J.
CORPORATE SOURCE: Tech. Univ., Berlin
SOURCE: Angew. Chem., Intern. Ed. Engl. (1966),
5(4), 420
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Diazoalkanes were converted by tert-BuOCl (I) in the presence of alcs.
into the corresponding acetals. The appropriate diazo-alkane (0.2 mol) in
dry Et₂O and 100 cc. dry suitable alc. treated dropwise with stirring at
-10° with 21.7 g. I yielded the corresponding RR'C(OR')₂ (R, R',
R'', and % yield given): H, H, Et, 70; H, H, Pr, 76; H, H, (R'R'' =)
CH₂CH₂, 57; Ph, H, Et, 49; Ph, Ph, Et, 43; (RR' =) 9-fluorenylidene, Et,
63.

IT 6397-78-0, Fluorene, 9-carbonyl-, diethyl acetal
(preparation of)

RN 6397-78-0 CAPLUS

CN 9H-Fluorene, 9-(diethoxymethylene)- (9CI) (CA INDEX NAME)



L18 ANSWER 20 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1966:27475 CAPLUS

DOCUMENT NUMBER: 64:27475

ORIGINAL REFERENCE NO.: 64:5060h, 5061a

TITLE: 4-(2-Piperidyl)-1,3-dioxolanes with local anesthetic,
spasmolytic, and central nervous system activity

AUTHOR(S): Hardie, W. R.; Hidalgo, J.; Halverstadt, I. F.; Allen,
R. E.

CORPORATE SOURCE: Cutter Lab., Berkeley, CA

SOURCE: Journal of Medicinal Chemistry (1966), 9(1),
127-36

CODEN: JMCMAR; ISSN: 0022-2623

DOCUMENT TYPE: Journal

LANGUAGE: English

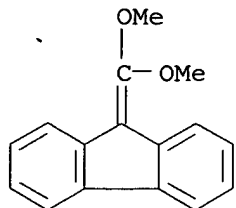
OTHER SOURCE(S): CASREACT 64:27475

AB A series of 2-(2-piperidyl)-1,4-dioxaspiro[4.5]decanes and
4-(2-piperidyl)-1,3-dioxolanes with alkyl and aryl substituents was
synthesized by the acid-catalyzed condensation of (2-piperidyl)-1,2-
ethanediol with ketones and acetals. The yields were best when using
acetals. Local anesthetic properties, generally with parallel
papaverine-like activity, were widely distributed through the series and
were most prominent when benzyl substituents were at the 2-position of the
dioxolane ring. Several compounds had the unique property of shortening
reaction time in the hotplate test. The spectrum of activities of one
compound, 2,2-diphenyl-4-(2-piperidyl)-1,3-dioxolane, led to the separation of
its racemates and the resolution of one of them.

IT 6861-54-7, Fluorene, 9-carbonyl-, dimethyl acetal
(preparation of)

RN 6861-54-7 CAPLUS

CN Fluorene, 9-carbonyl-, dimethyl acetal (7CI, 8CI) (CA INDEX NAME)



L18 ANSWER 21 OF 21 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1961:76032 CAPLUS

DOCUMENT NUMBER: 55:76032

ORIGINAL REFERENCE NO.: 55:14399d-i,14400a-b

TITLE: The stereochemistry of aromatic compounds. XI.
Experiments for the preparation of the anhydride of
1,9-fluorenedicarboxylic acid

AUTHOR(S): Kuhn, Richard; Breyer, Ursula

CORPORATE SOURCE: Max-Planck-Inst. Med. Forschung, Heidelberg, Germany

SOURCE: Chemische Berichte (1961), 94, 745-51

CODEN: CHBEAM; ISSN: 0009-2940

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

GI For diagram(s), see printed CA Issue.

AB cf. CA 49, 251i. Fluorene-1,9-dicarboxylic acid (I) could not form for steric reasons a normal anhydride which would have to be planar. I with Ac₂O yielded the planar enol lactone II (R = Me) (III) and with AcCl the planar cyclic acylal II (R = AcO) (IV). IV with bases lost the Ac groups to give orange solns. containing apparently the enol salt of the planar anhydride II (R = OH) (V). I (1 g.) and 10 cc. Ac₂O heated 2 hrs. at 150° yielded 720 mg. 1-methyl-3-oxo-2-oxa-2,3-dihydrofluoranthene (enol lactone of 9-acetylfluorene-1-carboxylic acid) (III), needles, m. 178-9° (EtOH); it sublimed without decomposition at 120°/0.0001 mm. III refluxed 0.5 hr. with 2N NaOH and acidified gave fluorene-1-carboxylic acid (VI), needles, m. 238°. III refluxed 2 hrs. with aqueous AcOH containing a little H₂SO₄ gave the 9-Ac derivative of VI, m. 205-10°. III with CrO₃ in AcOH yielded fluorenone-1-carboxylic acid (VII), m. 187-9°. I.0.5C₆H₆ (1 g.) refluxed about 2 hrs. with 15 cc. AcCl and evaporated, the residue dissolved in 25 cc. dry C₆H₆, treated with 50 cc. dry cyclohexane, and kept overnight at 0° gave 820 mg. IV, needles, m. 144-7° (C₆H₆-cyclohexane); it sublimed at 110°/0.0004 mm. with partial decomposition IV heated with aqueous alkali and acidified gave amorphous I, m. 232-9°. IV in C₆H₆ refluxed with excess PhNHNH₂ gave the monophenylhydrazide of I, m. 260-4°; the filtrate concentrated yielded PhNHNHAc, m. 124° (C₆H₆). IV refluxed about 20 min. with MeOH yielded 100% 9-Me ester (VIII) of I, m. 213-16°. IV treated at room temperature with absolute MeOH turned yellow and developed with a half-time of 11 min. 2 new characteristic bands, one at 400-520 mμ and an intense, steep band at 322 mμ; the disappearance of the visible band occurred with a half-time of about 100 hrs.; the spectrum approached more and more that of VIII. IV with MeOH and 1 volume-% 0.1N NaOH gave an immediate yellow color. IV with MeOH and 1 volume-% 0.1N HCl remained colorless and developed a spectrum, similar to that of VIII, with a half-time of about 1 hr. IV with iso-PrOH developed with a half-time of 1.5 hrs. the characteristic bands; the further solvolysis was slower than in MeOH. IV with dioxane and 0.05 volume-% Et₃N developed within a few min. the characteristic bands; the color decreased with a half-time of 2-3 hrs. I (500 mg.) in Me₂CO treated with 400 mg. dicyclohexylcarbodiimide in C₆H₆, filtered from precipitated dicyclohexylurea, m. 213°, concentrated, dissolved in Et₂O, and treated with CH₂N₂-Et₂O gave only a non-crystalline product. 9-Carbomethoxyfluorene (IX) (2 g.) in 30 cc. Et₂O treated with stirring under N with 0.3 cc. absolute MeOH and 400 mg. K, the mixture stirred over 2 hrs., and filtered, the unreacted K removed mech., and the filter residue treated dropwise in Et₂O with AcCl in Et₂O, filtered, and evaporated gave 500 mg. 9-Ac derivative of IX, m. 97° (cyclohexane). The infrared spectra of III and IV and the ultraviolet absorption spectrum of IV after 1.5 hrs. in MeOH were recorded.

IT 860215-12-9, Fluorene-1-carboxylic acid, 9-(dihydroxymethylene)-,
, acetate
(preparation of)

✓ RN 860215-12-9 CAPLUS

CN Fluorene-1-carboxylic acid, 9-(dihydroxymethylene)-, acetate (6CI) (CA
INDEX NAME)

